

CIPO
CANADIAN INTELLECTUAL
PROPERTY OFFICE

Ottawa Hull K1A 0C9

(21)	(A1)	2,161,059
(22)		1995/10/20
(43)		1996/04/22

- 6 (51) Int.Cl. CO8L 67/04; CO8L 101/00
- (19) (CA) APPLICATION FOR CANADIAN PATENT (12)
- (54) Thermoplastic Polymer Blends
- (72) Meier, Peter Switzerland;
  Bühler, Friedrich Switzerland;
  Fanelli, Raffaele Switzerland;
  Treutlein, Roland Switzerland;
- (71) Same as inventor
- (30) (DE) P 44 37 792.4 1994/10/21
- (57) 14 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.





# **Abstract**

The present invention discloses polymer blends on the basis of degradable aliphatic polyesters with melting points below 100°C, which can be processed in film blowing installations. The polymer blends are composed of aliphatic polyesters, polymeric auxiliary components and additives, wherein the percentages are selected such that they always add up to 100%. Processes for producing them and their use are also disclosed.

# **CASE 95-E515/CA**

# Thermoplastic Polymer Blends

The invention relates to thermoplastic polymer blends on the basis of degradable aliphatic polyesters with melting points below 100°C.

As a rule, aliphatic polyesters have a melting point below 100°C, mostly below 80°C, with molecular weights of less than 100.000 g/mol. The materials are soft and sticky and are therefore mostly employed as melt adhesives. They cannot be processed into blown film. If the polyester contains aromatic monomers, such a terephthalic or isophthalic acid, the melting point increases with the amounts added and the ability to produce blown films is improved. None of the polyesters with aromatic components are aliphatic polyesters and are therefore excluded. This applies to the preponderant number of polyesters. Because of their aromatic components they are not degradable.

The biodegradability of plastics is a further problem which has been strongly researched for a long time at great effort, because the ability of plastics to remain stable over long periods of time poses great ecological problems.

The majority of polymer materials for daily life and for industrial and agricultural applications are products which are produced from blown film. Unfortunately, plastics which can be worked into blown film, in particular in conventional blown film installations, display no biodegradability, while biodegradable plastics have up to now not been suitable for producing blown film.

However, there are many areas of use where the employment of biodegradable plastics makes sense, particularly where a total system becomes biodegradable because of this. Typical examples of this are compost bags and diapers.

Polycaprolactone (PCL) is an aliphatic polyester with a low melting point and is completely biodegradable.

Polycaprolactone is commercially available up to an average molecular weight of approximately 100.000 g/mol. However, none of the types are suitable for producing blown film directly. The production of films is only successful via the flat film process (*JP 05-105* 771, *JP 05-132 572*).

In connection with film production by means of a film blowing installation used for producing sacks and bags, the particular problem lies in the low melt stability of PCL and the low melting point which requires low processing temperatures.

Greater requirements are demanded in particular from the melt stability and the extensibility of the melt when producing blown films. The comparison between PE and PP should be noted as a known example for the differences in the suitability of blown films.

Other thermoplastic polymers must be added to achieve the required processing stability and economic production speeds. However, the amounts are important and must be selected such that the decomposition of the film material, for example in the compost, is not hampered.

One skilled in the art is aware that the production of flat films as well as fiber production from pure polycaprolactone already works.

Polymers blended with polycaprolactone with average gravimetric molecular weights of 70.000 are proposed for the production of stretched flat films in Patent Publication *JP 05-132 572 A2/1993*.

JP 04-148 918 A2/1992 describes the production of blown films with polycaprolactone P 767. It was noted that it was impossible to achieve the required melt stabilities as well as the required extensibility either P 767 with an Mn range around 50.000 or P 787 with an Mn range around 80.000. It is indeed possible to draw off a tubing within a very narrow processing window. However, the tubing cannot be blown open, so that the customary transverse stretching at ratios of 1:2 to 1:4 in relation to the nozzle cross section is not possible.

JP 05-132 572 A/1993 describes the production of polycaprolactones with average gravimetric molecular weights of 10.000 to 50.0000. Commercially available molecular weights lie maximally at 100.000 g/mol, which are unsuitable for blown film processing. It is not known whether higher molecular weights are suitable for producing blown films.

Furthermore, a substrate material for active lacquer and agricultural materials is described, for example, in *JP 57-185 344 A/1982*, with PCL as the substrate material, which is not produced as a blown film.

KR 93 01990 B describes an orthopedic bandage of PCL + filler + wax + EAA, whose manufacturing process has not been disclosed. As a rule such materials are thicker than 100 mm and are produced as flat foils. The effects of fillers on the blown film production is negatively judged here.

The product disclosed in *EP 0 535 994 A1* protects biodegradable flat foils of aliphatic PES (PCL) and starch, whose disadvantages are sensitivity to moisture and poor mechanical properties. There are no suggestions regarding blown film production.

*US Patent 4,912,174* recommends PCL and PU (diol + isocyanate) produced in situ for producing compressed plates of a thickness of 3 to 4 mm for orthopedic use. No suggestions are found regarding foil production and/or blown film suitability.

*US Patent 5,200,247* claims degradable flat foils of PCL + PVA, 75 - 90 / 25 - 10%, slot die extruded, cylinder temperature 350 to 450°F, extruder 2.5 inches, 65 rpm, 30 m per min., foil thickness 1 to 25 mil (1/1,000 in.), which are mechanically stretched.

Standard polymers, such as PE, PET, PS, PU, PVC, PP, PC are the main components, which are equipped with additives which increase degradability for improving degradability. Here, aliphatic polyesters are merely used as additives (biodegradable safening materials), so that the processing properties of the blends are derived from the main components.

Blown films are claimed in *WO 93/00399*, wherein the thermoplastic strength (TPS)(15 - 35%) is prescribed as a necessity. Poor mechanical properties and low water resistance as well as a strong effect of moisture on the mechanical properties result from this.

Blends with 60 - 90% PCL, 40 to 10% terpolymer with 60 to 80% styrene proportion and optionally 0 to 15% maleic acid anhydride for extrusion on Brabender 230°C, and again the production of plates for orthopedic use are claimed in WO 91/09909. The disclosure contains no suggestions as to foil suitability and no foil properties. Degradability is not of interest.

The products from *DE-OS 32 20 324* represent a synthetic resin mass, 100 parts PCL + 10 to 70 parts resin + 1 to 30 parts PVC. The intended use is as a core material for shoes. The main properties are bending resistance and stickiness, use as a pressed foil or hot melt and the production of pressed foils of a thickness of 1.4 mm. In every case the main property of stickiness has a negative effect on the tube separation in the production of blown films.

Thus, the prior art only shows the production of blown films of PCL with TPS. These products can be blown into films, however, they display great changes in their properties under the effect of moisture. Sealing properties become worse, tear resistance is reduced. Films below 20  $\mu$ m cannot be technically produced. The addition of TPS reduces the tear resistance and stretchability, so that it would always be necessary to use films of double thickness to obtain comparable resistance.

It is therefore the object of the invention to avoid the disadvantages of the previously sketched prior art and to make available molding materials on the basis of polyesters, which are per se unsuitable for blow molding, but which permit the manufacture of industrial products, in particular for agriculture and for daily life, in particular those which are biodegradable over a reasonable period of time, i.e. rot, as well as a process for their manufacture and their use.

The object of the invention is attained by means the use of thermoplastic polymer blends on the basis of degradable aliphatic polyesters with melting points below 100°C of the following composition:

<I> 50 to 94.99 weight-% of an aliphatic polyester or copolyester of at least one omega-lactone or at least one omega- hydroxycarboxylic acid with 4 to 12 C atoms, and/or of aliphatic diols with 2 to 12 C atoms and aliphatic dicarboxylic acids with 4 to 12 C atoms,

<II> 50 to 5 weight-% of at least one polymeric auxiliary component with polar groups, selected from the group of polyamides, polyurethanes, ethylenevinyl alcohol copolymers, ethylenevinyl acetate copolymers, ethylene acrylic acid copolymers, polyvinyl acetate, modified polyolefines, polystyrenes, polyacrylnitrils, polybutadienes, polyisoprenes, their copolymers and their mixtures, and

<III> 1 to 0.01 weight-% of at least one additive from the group of polar lubricants, polar waxes which are compatible with the components <I> and <II>, or silicic acid,

wherein the the components <I>, <II> and <III> always add up to 100 weight-%, and which are suitable for producing blown films,

wherein the blends selectively contain further auxiliary materials in accordance with the prior art.

It has now been surprisingly found that of the different polymeric auxiliary components only a few have sufficient compatibility with PCL to achieve the necessary melt stability for the production of blown films. It has also been surprisingly found that additional components are required to obtain high mechanical stability in the films.

Because of this low processing temperature of the aliphatic polyesters there is only a small temperature difference to the ambient temperature. The small temperature difference results in problems of heat dissipation, which cause strong instabilities of the tube and lead to blockage of the films. The attainment of the object is to find suitable components in particular with whose aid polyester and particularly PCL can be modified in such a way that films can be produced in film blowing installations.

Thus, put more succinctly, it is the object of the invention to provide molding materials suited for the production of blown film in the form of thermoplastic polymer blends, in particular on the basis of biodegradable plastic, namely aliphatic polyesters which as such cannot be produced by blow molding, in particular on the basis of lactones and/or polyesters on the basis of aliphatic dicarboxylic acids and diols and/or hydroxy carboxylic acids, their manufacture and their use.

The aliphatic polyesters <I> are biodegradable and are preferably composed of lactones and/or aliphatic dicarboxylic acids and diols and/or omega-hydroxy carboxylic acids, the polymeric auxiliary materials <II> contain polar groups, preferably have a melting point of below 170°C and are preferably selected from the group of polyamides, polyurethanes, ethylenevinyl alcohol copolymers, ethylenevinyl acetate copolymers, ethylene acrylic acid copolymers, polyvinyl acetate, modified polyolefines, as well as polystyrenes, polyacrylnitrils, polybutadienes, polyisoprenes, as well as their copolymers

and/or mixtures of the polymers and/or copolymers, and the additives <III> are selected from from the group of polar lubricants and/or waxes which are compatible with the aliphatic polyesters and/or copolyesters and/or are pyrogens or precipitated silicic acids, in particular silicic acid aerogels.

In addition to the 100% mentioned, the polymeric blends can contain customary auxiliary materials, such as dyes, fillers, flame-proofing agents, stabilizers, modifiers and the like.

The use of this class of polyesters is of particular interest for the manufacture of foils and films which can be further processed into, for example, compost bags, carrying bags or bags of all types, but also many other products, such as vegetable and fruit packaging, magazine and book packaging or, in cut-open form, as diaper film, in particular backing sheets for diapers, as wrapping or stretch films, stretch foils, shrink wrap, adhesive foils, laminated films, textile laminates, wood and paper coatings, metering bags, pest traps, carriers of active substances for horticulture and agriculture, as binder material for paper making, for producing molding materials with natural fibers, such as wood pulp, flax, ramie, wastepaper, and for modifying of degradable foam, expanded shaped products and loose fill, as melt adhesives for powder applications as well as the production of fibers, fabrics, non-wovens, in particular for industrial and agricultural use, as well as for producing twine, varns, binder cables for horticulture and agriculture, as blend components for modifying degradable materials, such as thermoplastic starch material, hydroxycarboxylic acid polyester, polyester amides, polyurethanes, cellulose molding materials, cellulose acetate molding materials, starch acetate molding materials, polyvinylpyrrolidone molding materials, polyester carbonate molding materials, and the like. The advantage of these products lies in that this type of material rots in the environment or in compost. Furthermore, an aliphatic polyester material which is suitable for films represents an ideal blend components for thermoplastic starches and other degradable polymers.

The process for manufacturing blends with auxiliary components, whose melting points are above 170°C, consists in that the polymeric auxiliary materials <II> and the additives <III) are pre-extruded with maximally 30 weight-% of polyester and are formed into pregranules, and in a second step these pre-granules are extruded with the remaining amount of polycaprolactone <I> to form the final granules.

The high-melting auxiliary components <II> and the additives <III> are preferably melted in the extruder (first half of the screw) and the polyester <I> is extruded into the melt via a side extruder (second half of the screw).

Also preferably, the pre-granules from step 1 are processed directly into blown films as a granule mixture with polycaprolactone or with other thermoplastic processable biodegradable granules.

Since the polycaprolactones of the types CAPA 650, CAPA 680 and Tone P 787 could not be processed into blown film, various granule mixtures and compounds were produced by means of twin-screw extruders. These granule mixtures and compounds were processed in a film blowing installation of the Collin company, tested for mechanical properties and the bag properties determined. Copolyamides with melting points between 80 and 160°C, ethylene acrylic acid copolymeres with melting points between 60 and 100°C, polyester urethanes preferably containing aliphatic polyester polyester diols and low-melting ethylene-vinyl alcohol copolymers with an ethylene content between 40 and 60 weight-% and which then have a melting range between approximately 150 to 170°C, are ideal blend components as added polymers <||>I|>.

Modified polyolefins, such as maleic acid anhydride, grafted polyethylenes (PE), polypropylenes (PP) or polycaprolactones (PCL), as well as polystyrenes (PS), polyacryl nitrils (PAN), polybutadienes (PB) and/or polyisoprenes (PI), as well as their copolymers can be used as promising polymeric auxiliary components <II>. Of particular interest are polyester, polyamide, copolyamide, polyurethane, in particular PU with polycaprolactone flexible segments. Since in only the fewest cases one component is sufficient, the mixtures with stepped compatibilities are mainly of interest.

An improvement in homogenity is achieved when polymers with similar melting points are pre-extruded together and are compounded in a second step or in the second half of the extruder srew with polycaprolactone. Granule production can take place directly if all components have melting points similar to polycaprolactone or if they are partially soluble in each other. In these cases even the production of films directly from the granule mixture is possible.

The polycaprolactone or other polyesters, i.e. aliphatic polyesters, which cannot be processed into blown films, are used in excess between 50 and < 95%, in particular between 75 and < 95%. The polymer additives necessary for processing are used at 5 to 50%, particularly at 25 to 5%. It is possible to employ lubricants of all types in weight proportions of 0.1 to 1% to reduce an adhesive tendency. Polyester waxes, polyamide waxes and polar waxes of natural origin are particularly effective.

The reduction of the separation problem of the film tube can be performed mechanically, for example by the addition of spherical mineral separating agents such as pyrogenic or precipitated silicic acid, in particular silicic acid aerogels, for example Aerosil and Silwett in amounts of 0.01 to 0.1 weigh-%. Mixtures of polycaprolactone and polyester urethane are of particular interest which, in a mixture of 84/16 weight-% have a brilliant transparent appearance after cold stretching of the blown films and can be employed above all in the field of flexible, highly transparent protective films. Biodegradable polycaprolactone and microbially "unstable" polyester urethane, in particular with polycaprolactone diol flexible

segments and aliphatic diisocyanate rigid segments, represent a technically high-value alternative for compostable films.

In place of isocyanate hard blocks which cross-link the elastomeric flexible segments thermoplastically, other block components capable of crystallization are advantageously usable, in particular polyester and polyamide with melting points above 100°C. Ideally, monomers are selected which have 2 to 6 C atoms between the ester and the amide groups.

If the extrusion of the aliphatic polyesters with the polyester urethanes or polyester amides is performed at higher temperatures, for example higher than 200°C. trans-esterification or trans-amidation processes can take place, so that the aliphatic polyesters can be built into the segmented block polymers. It is possible in this way to modify the material used in such a way that it has all desired properties. If granules are formed from it, the user can employ these directly for blow molding.

The following examples will explain the invention.

Formulation and processing examples are summarized in Tables 1 and 2. The components in parentheses were each pre- extruded and subsequently were directly processed into films in the form of a granule mixture together with the polycaprolactone.

In Example 18 the parentheses for ethylvinyl alcohol indicate that 80 weight-% ethylvinyl alcohol were pre-extruded together with 20 weight-% of glycerin.

#### Examples 1 to 3 (Table 1)

Polycaprolactone of the types CAPA 650, CAPA 680 and Tone P 787 are sequentially processed in a blown film installation. It was possible to achieve stable extrusion conditions in various temperature profiles in the range between 70 to 100°C for various extruder rpm and draw-off speeds. It was not possible to expand the film tube. If the nozzle temperature rises above 120°C, the melt stability at full cooling output is so small that the tubing tears under its own weight. At temperatures below 70°C the melt becomes wax-like and can no longer be blown open.

A special CAPA 650 modified by grafting with maleic acid anhydric for making the foil (Interrox company) was tested in Example 2b. The material also could not be blown open and is unsuitable for the production of blown film.

#### Examples 4 and 5 (Table 1)

The combination of ethylene acrylic acid polymer (EAA) (Primacor) and copolyamide (CoPA) (CF 6S) (EMS Chemie) processes well, but with slight homogeneity problems. Bags were produced to assess weldability. The bags were filled with compressed air and caused to burst. In the second test the bags were filled with water and the amount at which the bag bursts was measured.

5.10.95 / hkl

-.8.-

F: The film fails

N: The welding seam fails.

# Example 6 (Table 1)

The additional admixture of a polyester urethane component improves the homogeneity of the film, but results in considerable differences in strength in the linear and transverse directions. This variant processes excellently and is suitable for the production of blown films.

# Example 7 (Table 1)

EAA by itself is not capable to provide a usable degree of processibility to PCL. Distinct problems arise in the area of homogeneity and in particular of stability of the tube. Strong pulsations prevent the formation of blown film.

# Examples 8a and 8b (Table 1)

The combination of PCL and polyester urethane results in very satisfactory mechanical strength while completely utilizing the stretchability of PCL. Because of strong pulsations the tubing stability is insufficient.

In Example 8b the two components were pre-extruded and processed into a blown film in the second step. By means of this the tubing stability is clearly improved during processing, although the mechanical values drop slightly. Greater amounts of water were clearly handled in a bag filling test. This variant is particularly suitable for admixing with thermoplastic starch and at 20% (in relation to the total material) shows an extremely high tear propagation resistance in the linear direction of 460 N/mm in the dry state.

#### Example 9 (Table 2)

In addition to Lucalen (modified PE), polycaprolactone grafted with maleic acid anhydride was used. By means of this it is possible to create good compatibility of PCL with Lucalen. However, the problems in the area of tubing stability cannot be removed.

### Example 10 (Table 2)

Ethylenevinyl alcohol and two variants of polyester urethane are pre-extruded together with the amide wax Amide E and are subsequently extruded together with Tone P 787 as a granule mixture to form a foil. A very good processibility is achieved by means of this. The foils have very satisfactory linear and transverse strength along with very good bag properties. This compound is the especially prefered embodyment. In the water fill test a 30 µm film sealed to a bag can hold 17 liter of water.

5.10.95 / hkl

-.9.-

# Example 11 (Table 2)

CoPA (CF 6S), EVAL and a polyester urethane were pre-extruded and processed into a film as a granule mixture together with PCL. In spite of very good bag properties, problems in homogenity and stability of the tube occur. However, the final mechanical properties of this film are very good.

# Example 12 (Table 2)

Analogous to Example 10, but without pre-extrusion and without lubricants. This variant displays clear disadvantages in stability of the tube and has reduced mechanical properties in comparison with Example 10.

#### Examples 13 to 17 (Table 2)

In combination with EAA (Primacor 5980), Tone P 787 displays very good mechanical properties of the films, but because of its unstable behavior of the tube is not suitable for producing films. Examples 15 to 17 display unsatisfactory stability of the tube.

# Example 18 (Table 2)

Analogous to Example 10 and Example 12. In this case, 80 weight-% of ethylvinyl alcohol (EVOH) were pre-extruded together with 20 weight-% of glycerin and subsequently processed in the form of a granule mixture, together with the remaining components in accordance with Table 2, into blown film. Foil production proceeds very well, wherein high mechanical strength was obtained, together with a very high degree of tear propagation resistance, but a moderate water-fill result.

# Table 1

Example			23	2b	က	4	'n	9	7	88	8b
Capa 650 *standard*	%		100								
Capa 650 *Exper.*	%			100							
Capa 680	%	100									
Tone P787	%				100	83.4	83.4	76.1	83.3	83.4	(83.4)
CF6S	%					8.3	8.3	8.3			
Primacor 5980	%						8.3		15.7		
Primacor XU	%					8.3		8.3			
Lucalen A.2920.M	%										
EVAL E105	%										
Estane 58206	%										
Estane 64625	%							8.3		16.6	(16.4)
Armid E	%								0.5		
Sarmawax E34146	%								0.5		
B9429, P787 grafted	%										
B9430, P787 grafted	%										
srew speed	rpm	10	15	15	10	20	20		20	15	15
Current consumption	Y.	4.0	8.0	8.2	4,4	4.2	4.1		4.1	5.4	53
Material pressure	bar	220	180	130	160	150	160		152	194	310
Draw-in temp.	၁.	120	45	45	110	120	120		110	130	120
Material temp.	၁့	160	89	70	120	148	149		120	135	151
Nozzle temp.	ပ္	105	79	62	100	130	130	130	100	115	110
Draw-off speed	m/min	1.5	1.0	1.0	1.0	1.0	1.0		1.0	1.0	1.5
Roller pressure	bar	3.0	4.0	1.0	4.0	3.5	3.5	3.5	4.0	4.0	4.0
Foil thickness/width	um/mm	pul.	100/200	100/200	20/puls	15/360	50/360		65/puds	42/puls	30/300
Homogeneitiy		+	-	-	+	0	0	+	0	+	+
Stability of tube			•	•	-	+	-	+	-	-	+
Separation effect		+	+	+	+	+	+	+	+	+	0
Tear propag. resist.	i .Y/mm	230									280
Tensile strength at break, md	N/mm²	80			29	8+	09	63	93	7.1	57
Tensile strength at break, cd	N/mm <sup>2</sup>	22			18	22	28	16	33	61	39
Elongation at break, md	%	810			170	820	810	1050	1300	1170	830
Elongation at break, cd	%	570			360	069	550	099	086	1080	088
Weldabiliy	Beam	:	+	+	+	+	+	+	+	+	+
Air blowing test	Fail		ж	Y.	Į.	(±,	íz.	Œ.	ſī.	SE-	íz,
Water fill test	Liter		S/N	X.	SF	20/F	17/F	18/F	4/F	7/F	14/F

# Table 2

Example		6	10	11	12	13	14	15	16	1.7	18
Capa 650 *standard*	%										
Capa 650 *Exper.*	%										
Capa 680	%										
Tone P787	%	75.1	75.1	75.1	75.1	83.4	75.0	(83.4)	75.1	8.98	75.1
CF6S	%			(8.3)				(8.3)	(8.3)	(8.3)	
Primacor 5980	%	8.3				16.6	25.0				
Primacor XU	%									(8.3)	
Lucalen A.2920.M	%	8.3									
EVAL E105	%		(8.3)	(8.3)	8.3				(8.3)	(8.3)	(8.3)
Estane 58206	%		(8.3)		8.3						8.3
Estane 64625	%		(7.8)		8.3			(7.8)	(7.8)	(8.3)	8.3
Armid E	%		(0.5)					(0.5)	(6.5)		
Sarmawax E34146	%										
B9429, P787 grafted	%										
B9430, P787 grafted	%	8.3									
srew speed	rpm	10	10	10	7	20	10	20	ů.	10	12
Current consumption	Y	2.6	1.7	4.5	2.8	4.9	3.6	4.1	3.0	3.3	4.2
Material pressure	bar	75	109	109	26	186	123	80-360	75	82	240
Draw-in temp.	ပ္စ	110	120	120	140	100	120	95	120	120	140
Material temp.	ပ္	128	151		188	120	121	113	158	155	187
Nozzle temp.	ပ္	100	135		155	95	100	100	135	135	125
Draw-off speed	m/min	1.0	1.5		1.0	1.2	1.2	1.5	1.6	3.0	1.6
Roller pressure	bar	4.0	4.0		3.0	1.0	4.0	4.0	4.0	4.0	3.0
Foil thickness/width	mm/mm	25/puls	30/320	20/360	20/300	55/380	50/puls		15/380	15/400	2500
Homogeneitiy		+	+		+	0		0	0	+	+
Stability of tube		+	+		0	•	:	•		0	+
Separation effect		+	+	+	+	+	+	•	+	+	+
Tear propag. resist.	. V/mm		330		200-275						370
Tensile strength at break, md	N/mm²	35	64	45	33	52	30		18	30	75
Tensile strength at break, cd	N/mm²	15	7	50	21	31	19		36	28	32
Elongation at break, md	%	840	750	260	590	1150	009		290	560	590
Elongation at break, cd	%	09+	630	750	520	790	610		550 550	<b>\$</b>	969
Weldabiliy	Beam	+	+	+	+	+	ち	+	+	+	+
Air blowing test	Fail	[E4	í24	Ŀ	E.	Œ,	Ŧ.	Œ	Ħ	îs,	Œ
Water fill test	Liter	12/F	17/F	10/F	6/F	10/F	3/F	1	1	7/F	10F
	-										1

The plastic materials employed in these examples and listed in Tables 1 and 2, where they are identified by their commercial designations, are identified in detail as follows:

PCL	Polycaprolactone	Mn 50 000 - 100 000
Starch material	thermoplastic starch granules	
PE	Polyethylene	Commercially available
PP	Polypropylene	Commercially available
PS	Polystyrene	Commercially available
PAN	Polyacrylnitril	Commercially available
PB	Polybutadiene	Commercially available
PI	Polyisoprene	Commercially avaiable
PU	Polyurethane	Commercially available
EAA	Polyethylenacrylic acid	Commercially available
CoPA (CF6S)	Copolyamide 6/12 (EMS-Chemie)	Commercially available
EVAL=EVOH	Ethylenvinyl alcohol	Ethylene content 44 %

CAPA 650	Polycaprolactone	Mn 50 000 g/mol
CAPA 650 *Exp*	Polycaprolactone	Modifier (Interox)
CAPA 680	Polycaprolactone	Mn 80 000 g/mol
TONE P787	Polycaprolactone	Mn 80 000 - 100 000 g/mol
CF6S	Copolyamide 6/12	EMS-Chemie
Primacor 5980	Ethylenacrylic acid	DOW
Primacor XU	Ethylenacrylic acid	DOW
Lucalen A2920M	Polyethylene grafted	BASF
EVAL E105	Ethylenevinyl alcohol (44% ethylene)	Kuraray
Estane 58206	Polyesterurethane	Goodrich
Estane 54625	Polyesterurethane	Goodrich
Armid E	Armide	Akzo
Sarmawax E34146	Typ of wax unknown	Sandoz/Italy
B9429, P787	Polycaprolactone graftet (maleic acid	EMS-Chemie
B9430, P787	anhydride)	EMS-Chemie

# <u>Claims</u>

1. Thermoplastic polymer blends on the basis of degradable aliphatic polyesters with melting points below 100°C,

#### characterized in that

they are prepared from the following components:

<|> 50 to 94.99 weight-% of an aliphatic polyester or copolyester of at least one omega-lactone or at least one omega-hydroxycarboxylic acid with 4 to 12 C atoms, and/or of aliphatic diols with 2 to 12 C atoms and aliphatic dicarboxylic acids with 4 to 12 C atoms,

<II> 50 to 5 weight-% of at least one polymeric auxiliary component with polar groups, selected from the group of polyamides, polyurethanes, ethylenevinyl alcohol copolymers, ethylenevinyl acetate copolymers, ethylene acrylic acid copolymers, polyvinyl acetate, modified polyolefines, polystyrenes, polyacrylnitrils, polybutadienes, polyisoprenes, their copolymers and their mixtures, and

<III> 1 to 0.01 weight-% of at least one additive from the group of polar lubricants, polar waxes which are compatible with the components <I> and <II>, or silicic acid,

wherein the the components <!>, <!!> and <!!!> always add up to 100 weight-%, and which are suitable for producing blown films,

wherein the blends selectively contain further auxiliary materials in accordance with the prior art.

2. Polymer blends in accordance with claim 1,

### characterized in that

the auxiliary materials are selected from the group of dyes, fillers, flame-proofing agents, stabilizers.

3. A method for producing the polymer blends in accordance with claim 1 or 2, characterized in that

in a first step the auxiliary components with melting points above 150°C are mixed with the additives <III> and selectively with a small amount of the polyester <I> of maximally 30 weight-% of the total amount of polyester and are extruded into pregranules and in a second step are extruded with the polyester <I> or its remaining amount into final granules, which subsequently is directly further processed or is extruded and granulated before being processes further.

-.14.-

4. A method in accordance with claim 3, characterized in that

in the second process step the polyester <I> is fed into the melt mix from the first process step via a separate melting unit.

- A method in accordance with claim 4, characterized in that the melting unit is an extruder.
- A method in accordance with one of claims 3 to 5,
   characterized in that
   further processing takes place with the addition of at least one further polymer
- 7. A process in accordance with claim 6, characterized in that further polymers can be biodegraded and thermoplastically processed.
- 8. A process in accordance with one of claims 3 to 7, characterized in that the final granules are directly processed into blown film.
- 9. Use of the Polymer blends in accordance with one of claims 1 or 2 for producing blown foils, in particular those which are used for bags of all types, in particular compost sacks, carrying bags, as well as vegetable and fruit packaging, magazine and book packaging, as metering bags, pest traps, carriers of active substances for horticulture and agriculture or, in cut-open form, as diaper foil, in particular backing sheets for diapers, as wrapping or stretch films, stretch foils, shrink wrap, for producing adhesive films, laminated films, textile laminates, wood and paper coatings.
- 10. Use of the polymer blends in accordance with one of claims 1 or 2 for producing fibers, fabrics, non-wovens, for industrial and agricultural use, as well as for twine, yarns, binder cables, in particular for horticulture and agriculture.
- 11. Use of the polymer blends in accordance with one of claims 1 or 2 as blend components for modifying degradable materials, such as thermoplastic starch material, hydroxycarboxylic acid polyester, polyester amides, polyurethanes, cellulose molding materials, starch acetate molding materials, polyvinylpyrrolidone molding materials.

-.15.-

- 12. Use of the polymer blends in accordance with one of claims 1 or 2 as binder material for paper making, for producing molding materials with natural fibers, such as wood pulp, flax, ramie, wastepaper.
- 13. Use of the polymer blends in accordance with one of claims 1 or 2 for producing and/or modifying degradable foam, expanded shaped products and loose fill.
- **14.** Use of the polymer blends in accordance with one of claims **1** or **2** as melt adhesives for powder applications.